

# Reaction product-driven restructuring and assisted stabilization of a highly dispersed Rh on ceria catalyst

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## Abstract

Understanding the structural dynamics of a catalyst under reaction conditions is challenging but crucial for designing catalysts. By combining *in situ/operando* characterization and first principles modelling, here we show that supported Rh catalysts undergo restructuring at the atomic scale in response to carbon monoxide, a gaseous product formed during the steam reforming of methane. Despite the transformation of the initially prepared single Rh cation catalyst into large Rh particles during hydrogen pretreatment, the formed Rh particles re-disperse to low-nuclearity CO-liganded Rh clusters,  $\text{Rh}_m(\text{CO})_n$  ( $m=1-3$ ,  $n=2-4$ ) under catalytic conditions. Theoretical simulations under reaction conditions suggest that the pressure of CO product stabilizes  $\text{Rh}_m(\text{CO})_n$  sites, while *in situ/operando* spectroscopy reveals a reversible restructuring between  $\text{Rh}_3(\text{CO})_3$  clusters and Rh nanoparticles driven by CO pressure. The findings demonstrate the significance of including product molecules in the atomic-scale understanding of catalytic active sites and mechanisms.

Heterogeneous catalysts, commonly formed by particles of active metals deposited on a high surface area support, are of central importance for chemical production and energy transformation. Controlling the structure of a heterogeneous catalyst's active sites is critical to maintaining its activity.<sup>1,2</sup> The surface composition and morphology of a catalyst can be strongly affected by the reaction environment, such as the change in the reducing or oxidizing capability of a reactant gas or of the temperature.<sup>3-5</sup> At high temperature, oxide-supported metal nanoparticles can sinter,<sup>6,7</sup> and even the oxide support can undergo a phase transition.<sup>8</sup> At the atomic scale, a catalytic reaction event typically occurs on a specific site, consisting of one or more atoms of the metal particle and potentially involving atoms of the support at the metal particle's periphery, at a given temperature in the gaseous environment. To optimize the use of precious metals, a large effort has been made recently to create highly dispersed supported catalysts, in the form of small clusters.<sup>1</sup> Downsizing to the single atom extreme has significantly benefited structurally insensitive catalytic reactions that occur on large metal particles;<sup>1,2,9,10</sup> however, these catalysts can be strongly susceptible to sintering during reaction.<sup>11</sup> Therefore, understanding the structural dynamics of a highly dispersed supported catalyst under a specific catalytic environment and determining factors that maintain the high dispersion are crucial to the rational design of efficient and robust heterogeneous catalysts.

Here we report the evolution of coordination and chemical environments of initially prepared singly dispersed Rh atoms anchored on CeO<sub>2</sub> (Rh<sub>1</sub>/CeO<sub>2</sub>) driven by the reduction pretreatment step of the catalyst and then by the catalytic conditions to demonstrate the predominant impact of the partial pressure of a product gas on the formation and preservation of highly dispersed Rh<sub>m</sub> (m=1-3) cluster active sites during catalysis. We find that although the freshly prepared Rh<sub>1</sub> single atoms anchored on CeO<sub>2</sub> (Rh<sub>1</sub>/CeO<sub>2</sub>) transform into Rh nanoparticles

(Rh NP/CeO<sub>2</sub>) after H<sub>2</sub> reduction pretreatment, the CO generated by the steam reforming of methane (SRM) reaction ( $CH_4 + H_2O \rightarrow CO + 3H_2$ ) breaks down the Rh NPs into highly dispersed sub-nanometer CO-liganded Rh sites, Rh<sub>m</sub>(CO)<sub>n</sub> (m=1-3, n=2-4). The restructuring of this catalyst is uncovered by combining *in-situ/operando* studies and first principles modelling, addressing the hidden evolution of catalytic sites at atomic scale driven by pressure of product gases.

## Results

### Structural evolution of the Rh/CeO<sub>2</sub> catalyst

Transmission electron microscopy (TEM) and X-ray diffraction (XRD) studies confirmed the crystallization of CeO<sub>2</sub> in the as-synthesized 0.17wt% Rh/CeO<sub>2</sub> catalyst as seen in Supplementary Figures 1 and 2. The studies show that neither metallic Rh nor Rh<sub>2</sub>O<sub>3</sub> nanoparticles formed in the as-synthesized catalyst. Coordination and chemical environments of Rh atoms of the as-synthesized catalyst were examined with X-ray absorption near-edge spectroscopy (XANES), extended X-ray absorption fine structure (EXAFS), ambient-pressure X-ray photoemission spectroscopy (AP-XPS) and diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS). The energy position of the Rh K-edge of the as-synthesized catalyst in XANES (black line in Supplementary Figure 3a) resembles that of the Rh<sub>2</sub>O<sub>3</sub> reference (blue line in Supplementary Figure 3a), suggesting that the Rh atoms of the as-synthesized catalyst are cationic. The Fourier transformed *r*-space EXAFS spectrum at the Rh K-edge for the as-synthesized catalyst indicates that Rh atoms are singly dispersed (Figure 1a). There is only one major peak at 2.03 Å observed in the range of 0-4 Å. All distances or bond lengths in this report are values after phase correction of EXAFS. On average, 6.73±0.4 oxygen atoms in the 1<sup>st</sup> coordination shell of a Rh atom

contribute to the peak at 2.03 Å (Supplementary Table 1). The black dashed line in Figure 1a marks the distance between two Rh atoms in the second shell [Rh-(O)-Rh] of Rh<sub>2</sub>O<sub>3</sub> (2.87 Å). The lack of a second shell of Rh atoms in Figure 1a further demonstrates the absence of Rh<sub>2</sub>O<sub>3</sub> NPs in the as-synthesized catalyst. Hence, the *r*-space spectrum of Rh K-edge of the as-synthesized catalyst suggests that Rh atoms are singly dispersed Rh cations. The high Rh-O coordination number indicates that the Rh<sub>1</sub> cations are substituted for Ce cations in the surface lattice of CeO<sub>2</sub>. The single-atomic dispersion of Rh<sub>1</sub> cations is further supported by DRIFTS with CO as a chemical probe. The observed peaks at 2085 and 2017 cm<sup>-1</sup> (Supplementary Figure 4) are assigned to symmetric and asymmetric vibration of geminal Rh<sub>1</sub>(CO)<sub>2</sub>, respectively.<sup>12,13</sup> The lack of bridge-adsorbed CO in the window of 1850-1900 cm<sup>-1</sup> excludes the existence of Rh-Rh metallic bonds, in line with the formation of singly dispersed Rh<sub>1</sub> cations.<sup>14-16</sup> Thus, in the following paragraphs, both 0.17wt% Rh/CeO<sub>2</sub> and Rh<sub>1</sub>/CeO<sub>2</sub> will be interchangeably used to denote the as-synthesized catalyst.

During pretreatment, the Rh<sub>1</sub>/CeO<sub>2</sub> was treated in 5% H<sub>2</sub> at 500 °C. The surface chemistry of this catalyst during this pretreatment was tracked with AP-XPS (Figures 2a and 2b). The deconvolutions of Ce 3d and O 1s spectra are described in the Supplementary Note 2 and 3. The observation of the peak at 532.0 eV in the O 1s spectrum assigned to the O\* atom of H'-O\*-Ce<sup>3+</sup>-O (Figure 2b) implies that Rh atoms catalyze the dissociation of molecular H<sub>2</sub> to atomic H' (': guest), which reduces Ce<sup>4+</sup> to Ce<sup>3+</sup> by bonding to O<sub>surf</sub>\* atoms on the CeO<sub>2</sub> surface to form H'-O\*-Ce<sup>3+</sup>-O.

The reduction of the catalyst by H<sub>2</sub> markedly changes the coordination environment of Rh atoms in Rh<sub>1</sub>/CeO<sub>2</sub>. Upon reduction, a new peak at 2.66 Å forms in the Fourier transformed *k*<sup>2</sup>-weighted *r*-space EXAFS spectrum, while the Rh-O peak at 2.05 Å weakens. This peak is assigned

to Rh-Rh metal bonds (Figure 1b, see also ex-situ spectra in Supplementary Figure 5). On average,  $5.7 \pm 0.7$  Rh atoms in the first shell of a Rh atom contribute to the peak at  $2.66 \text{ \AA}$  (Supplementary Table 1). The approximate size of these Rh NPs is about 1.0 nm based on the reported dependence of average Rh-Rh coordination number on the size of a Rh NP.<sup>17</sup>

After  $\text{H}_2$  reduction, the Rh NP/ $\text{CeO}_2$  catalyst again significantly restructures under SRM conditions at  $500 \text{ }^\circ\text{C}$  in a feed stream of a mixture of 2.5 ml/min  $\text{CH}_4$  and 22.5 ml/min He, bubbled through water at  $25 \text{ }^\circ\text{C}$ . The catalytic performance of  $\text{Rh}_1/\text{CeO}_2$  catalyst is shown in Supplementary Figure 6. Compared to the  $r$ -space spectrum of Rh NPs formed by  $\text{H}_2$  reduction (Figure 1b), the spectrum during catalysis exhibits distinctly different features (Figure 1c, see also Supplementary Figure 7 for Rh and  $\text{Rh}_2\text{O}_3$  reference spectra). This spectrum consists of a primary peak at  $2.04 \text{ \AA}$  assigned to Rh-O bonds and a relative weak peak at  $2.57 \text{ \AA}$  assigned to Rh-Rh bonds (Supplementary Table 1). Compared to the spectrum under reduction condition (Figure 1b), the intensity of the peak of Rh-Rh bonds during catalysis (Figure 1c) is largely weakened, while the intensity of the peak of Rh-O is simultaneously increased. The coordination number of Rh to Rh [CN(Rh-Rh)] and that of O to Rh [CN(O-Rh)] under the catalytic environment are 1.4 and 5.3 respectively (Supplementary Table 1). The ratio of CN(Rh-Rh) to CN(O-Rh), 1.4/5.3, during catalysis at  $500 \text{ }^\circ\text{C}$ , is only 0.04 of the ratio,  $5.7/0.87$ , of the catalyst under 5%  $\text{H}_2$  at  $500 \text{ }^\circ\text{C}$ . The distinct differences in CN(Rh-Rh) and CN(O-Rh) show that the Rh NPs formed under  $\text{H}_2$  reduction are redistributed under the catalytic environment. Notably, the average CN(Rh-Rh) during catalysis at  $500 \text{ }^\circ\text{C}$  is 1.4 (Supplementary Table 1), suggesting the formation of  $\text{Rh}_2$  dimers whose CN(Rh-Rh) is 1.0 and/or  $\text{Rh}_3$  triangular clusters whose CN(Rh-Rh) is 2.0. The significant change of the Rh atoms' coordination environment upon switching from reduction to catalysis conditions is supported by the Wavelet transformation of the EXAFS Rh K-edge spectra (WT-EXAFS) of the

catalyst. For the reduced catalyst (Supplementary Figure 8a), a major maximum in the WT-EXAFS plot is found at  $R=2.30 \text{ \AA}$  (distance before phase correction), which is assigned to metallic Rh-Rh coordination of Rh metal NPs based on the reference sample of a metallic Rh foil (Supplementary Figure 8d). However, the maximum of WT-EXAFS of the catalyst during catalysis (Supplementary Figure 8b) is different from either the maximum of the Rh-O coordination in  $\text{Rh}_2\text{O}_3$  NPs (Supplementary Figure 8c) or that of Rh-Rh coordination of Rh metal NPs (Supplementary Figure 8a), suggesting that the coordination environment of Rh during catalysis is different from either  $\text{Rh}_2\text{O}_3$  or Rh metal NPs. Clearly, the chemical and coordination environments of Rh atoms indicate a second restructuring; the Rh NPs re-disperse into smaller Rh clusters which represent the steady state active sites of the catalyst.

Along with the re-dispersion of 1.0 nm Rh nanoparticles to  $\text{Rh}_2$  dimer/ $\text{Rh}_3$  trimer structures under catalytic conditions, the surface chemistry of the  $\text{CeO}_2$  support of this catalyst experiences an obvious change as well, with the formation of surface hydroxyl groups and the reduction of the surface  $\text{Ce}^{4+}$  cations. During catalysis ( $P_{\text{CH}_4} = 0.5 \text{ Torr}$  and  $P_{\text{H}_2\text{O}} = 1.0 \text{ Torr}$ ), a peak at  $\sim 531 \text{ eV}$  is seen after de-convolution in the O 1s XPS spectrum (blue peak in Figure 2d and Supplementary Table 2), assigned to surface OH groups, while the blue peak is absent under reduction at  $500 \text{ }^\circ\text{C}$  (Figure 2b). Such H'O'- $\text{Ce}^{3+}$ -O hydroxyl groups (blue peak in Figure 2d) can be readily formed through dissociation of reactant  $\text{H}_2\text{O}$  in the environment of the SRM reaction. This is consistent with our thermodynamics calculations based on density functional theory (DFT), which suggest that  $\text{CeO}_2(111)$  is hydroxylated during catalysis, and the topmost  $\text{Ce}^{4+}$  cations of the  $\text{CeO}_2$  surface are reduced to  $\text{Ce}^{3+}$  under the realistic  $\text{H}_2$  and  $\text{H}_2\text{O}$  pressures experienced by the catalyst during steady state SRM at  $500 \text{ }^\circ\text{C}$  (Figure 3).  $\text{CeO}_2(111)$  was chosen as the facet to build the structural models for computational studies as the (111) facet is the main surface exposed on  $\text{CeO}_2$

nanoparticles (Supplementary Figure 1b). The insensitivity of the predicted surface structure to the choice of  $U_{eff}$  as well as DFT-based spectroscopic calculations further support the presence of surface hydroxyls on the CeO<sub>2</sub> support under catalytic conditions (Supplementary Note 11 and Supplementary Figures 10-25).

### **Atomic scale understanding of active site stabilization**

The experimentally observed structural evolution at the atomic scale of Rh-based catalytic sites during catalysis is explained by our atomistic modeling. Using DFT calculations, we computed the structures of Rh<sub>1</sub>, Rh<sub>2</sub>, and Rh<sub>3</sub> active sites, with H, OH and CO as possible ligands generated during catalysis. We considered a large number of liganded cluster structures (more than 500) on the hydroxylated CeO<sub>2</sub>(111) surface, including structures with an O vacancy surrounding the Rh site; we found the formation of such an O vacancy to be exergonic in the presence of Rh. By holding the chemical potentials of H<sub>2</sub> and H<sub>2</sub>O constant, the influences of CO pressure ( $P_{CO}$ ) and temperature on the structure and composition of the clusters were explored through atomistic thermodynamics (Figure 4).

Under the steady state catalytic conditions at 500 °C (Figure 4a), we find that ensembles of distinct CO-liganded Rh clusters are generated, including low energy metastable ones (Figure 5, Supplementary Note 12).<sup>18</sup> Rh<sub>3</sub>(CO)<sub>3</sub> is the most stable and hence most probable cluster based on our calculations of the Gibbs free energy of formation. In the ensemble of Rh active site structures, the Rh<sub>3</sub>(CO)<sub>3</sub> sites are more stable than both Rh<sub>2</sub>(CO)<sub>3</sub> and Rh<sub>1</sub>(CO)<sub>2</sub> (Figure 5); thus, the Rh trimers likely make up the majority of the active sites. Consistent with the reaction-driven redispersion of Rh nanoparticles uncovered experimentally, the thermodynamic calculations



suggest that small Rh<sub>2</sub>/Rh<sub>3</sub> clusters can be stabilized by interaction with CO, a product of SRM. When comparing the stability of these small trimers to larger Rh nanoparticles (NP), we found that the SRM reaction condition at 500 °C, marked with a green cursor, lies next to the phase boundary between the stability domain of the Rh NPs and of the CO-liganded Rh sites, Rh<sub>m</sub>(CO)<sub>n</sub> (Figure 4b).

Although our thermodynamic analyses have identified that the reaction-generated CO are crucial for the stabilization of small Rh clusters, the influence of the CeO<sub>2</sub> support cannot be understated. Numerous studies have shown that the nature of the catalyst support surface in a reactive environment strongly affects the structure of supported metal atoms and nanoparticles.<sup>16,19-</sup>

<sup>21</sup> To assess the role of the support, we calculated the reaction internal energy to form Rh<sub>3</sub>(CO)<sub>3</sub> from a free Rh<sub>3</sub> cluster and three CO molecules on one hydroxylated surface containing 5.09 OH/nm<sup>2</sup> without O<sub>vac</sub> (Region 1B in Figure 3a, also Supplementary Figure 27a) and one containing 5.09 OH/nm<sup>2</sup> with 0.85 O<sub>vac</sub>/nm<sup>2</sup> (Supplementary Figure 27b). The reaction energies for the formation of Rh<sub>3</sub>(CO)<sub>3</sub> were found to be -10.58 eV and -10.90 eV, respectively. This difference suggests that the presence of an O vacancy renders the reaction energy for the formation of Rh<sub>3</sub>(CO)<sub>3</sub> slightly more favorable by 0.11 eV/Rh. We further compared the interaction energy between the Rh<sub>3</sub>(CO)<sub>3</sub> cluster and the support CeO<sub>2</sub>(111) surface (Supplementary Figure 27c), which was found to be -8.03 eV, to the interaction energy between the Rh<sub>3</sub>(CO)<sub>3</sub> cluster and the support CeO<sub>2</sub>(111) surface with an O vacancy in the Rh<sub>3</sub>(CO)<sub>3</sub>'s vicinity (Supplementary Figure 27d), which was found to be -6.63 eV. These interaction energies are calculated by detaching the cluster from the surface without any structural relaxation of the obtained fragments. The existence of an O vacancy hence in contrast weakens the interaction energy by 0.47 eV/Rh atom, but allows the cluster and surrounding support atoms to adopt a less deformed, intrinsically more stable,

configuration. As a net result, the oxygen vacancies of CeO<sub>2</sub> surface can cooperate with the CO ligands to slightly stabilize the formation of small Rh<sub>3</sub>(CO)<sub>3</sub> clusters.

### **Pressure-dependent formation of Rh<sub>m</sub>(CO)<sub>n</sub> clusters**

The formation of Rh<sub>m</sub>(CO)<sub>n</sub> clusters is also observed by two *operando* DRIFTS experiments (Figure 6b and Supplementary Figure 9b). Figure 6b includes three series of experiments. In series 1 (Figure 6b, b1-b9), a pulse of CH<sub>4</sub> was added to the flowing Ar carrying the water vapor while the pre-reduced catalyst was held at 500 °C in the mixture of Ar and water vapor. During the pulse, the feed stream consists of ~1% CH<sub>4</sub> and ~3% H<sub>2</sub>O. The CO produced from the steam reforming of CH<sub>4</sub> in terms of the reaction between the CH<sub>4</sub> pulse and flowing H<sub>2</sub>O vapor, forms Rh<sub>3</sub>(CO)<sub>3</sub>. In the first minute after the CH<sub>4</sub> pulse was introduced to the DRIFTS cell, there were no vibrational features in the region of 2050-1900 cm<sup>-1</sup> as the SRM had just started to produce CO (Supplementary Figure 9b, b0). Vibrational features at 2012 cm<sup>-1</sup> and 1930 cm<sup>-1</sup> in the region of 2050-1900 cm<sup>-1</sup> were abruptly observed 2 minutes after the pulse, showing the formation of Rh<sub>m</sub>(CO)<sub>n</sub> species (Figure 6b, b1, see also Supplementary Figure 9b, b1). These observed vibrational features are in good agreement with the two highest CO stretching frequencies at 1982 cm<sup>-1</sup> and 1939 cm<sup>-1</sup> for Rh<sub>3</sub>(CO)<sub>3</sub> calculated by DFT (Supplementary Figure 28). As no external source of CO was introduced to the *operando* DRIFTS experiment (Figure 6b, b1-b9 and Supplementary Figure 9b), the formation of Rh<sub>m</sub>(CO)<sub>n</sub> must be driven by the CO product from SRM at 500 °C.

Thermodynamic stability calculations of the Rh active site show that the ligand structure of the Rh active site is sensitive to the CO chemical potential. Starting from the steady state catalytic environment (Figures 4a and 4b) with Rh<sub>3</sub>(CO)<sub>3</sub> as the most stable species (Figure 4e),

two ligand restructuring events (labeled 1 and 2 and marked with left pointing arrows in Figure 4a) may occur when  $P_{CO}$  is decreased while the temperature is held constant at 500 °C. In these two events at 500 °C, the active site loses CO ligands. In event 1, one CO ligand is lost when  $P_{CO}$  falls below  $10^{-3}$  bar, forming  $Rh_3(CO)_2$  (Figure 4d). Event 2 occurs when  $P_{CO}$  falls below  $10^{-5}$  bar, where the  $Rh_3(CO)_2$  site loses its remaining CO ligands to form the  $Rh_3H_1$  site (Figure 4c). If the pressure of CO was increased starting from steady state condition, one additional CO is predicted to attach to the  $Rh_3(CO)_3$  site when  $P_{CO}$  rises above  $10^{-1}$  bar, forming the  $Rh_3(CO)_4$  site (Figure 4f). Importantly, both the  $Rh_3(CO)_2$  and  $Rh_3H_1$  sites are metastable compared to the Rh nanoparticle, while the  $Rh_3(CO)_3$  and  $Rh_3(CO)_4$  are similarly stable (Figure 4b). This difference among thermodynamic stabilities in Figure 4a underlines the key role of CO on the stability of the Rh active site. The predicted  $P_{CO}$ -dependent restructuring is consistent with a theoretically predicted decreasing trend in the frequency of the principal CO stretching mode, along the order of  $Rh_3(CO)_4 > Rh_3(CO)_3 > Rh_3(CO)_2$  (Supplementary Note 13 and Supplementary Figure 28).

The predicted  $P_{CO}$ -dependent restructuring of the catalytic sites at 500 °C was also experimentally observed by *operando* DRIFTS studies, where CO was produced by the reaction between the flowing  $H_2O$  vapor and pulsed  $CH_4$  at 500 °C. In series 1 of Figure 6b,  $CH_4$  was only provided through a pulse; thus, no more CO was continuously produced. Since water vapor was continuously flowing through catalyst, the partial pressure of CO (and the chemical potential of CO) around the catalyst progressively decreased. The time-dependent vibrational signatures show that the  $Rh_3(CO)_3$  clusters progressively restructure to CO-ligand-free Rh clusters as illustrated in Figure 6a (Series 1). The transformation of  $Rh_3(CO)_3$  to a CO-ligand-free Rh cluster was evidenced by the evolution of CO vibrational feature. The CO stretching frequencies of  $Rh_3(CO)_3$  obviously

shift to lower values, and their intensities decrease along the decrease of CO pressure (Figure 6b, b1-b9), as marked with the red arrows in Figure 6b, b1-b9 (see also Supplementary Figure 9).

The key role of CO in maintaining the highly dispersed  $\text{Rh}_3(\text{CO})_3$  catalytic sites was further confirmed by the reversible restructuring of the Rh site observed in two additional series of experiments in Figure 6b. Upon the disappearance of  $\nu(\text{CO})$  peaks in the range of 2050-1850  $\text{cm}^{-1}$  at 500 °C (Figure 6b, b9), Rh clusters without CO ligand form at the end of Series 1. Once CO was introduced to the catalyst as a steady flow (at the 31<sup>st</sup> min, 1% CO), the Rh clusters immediately restructured to  $\text{Rh}_3(\text{CO})_3$  (Spectrum b10 in series 2 of Figure 6b). This restructuring is evidenced by the immediate reappearance of  $\nu(\text{CO})$  peaks at 2010  $\text{cm}^{-1}$  and 1920  $\text{cm}^{-1}$  in Series 2 (Figure 6b, b10). The produced structure experiences nearly no change as long as CO is continuously flowing through the catalyst (Figure 6b, b10-b14). Notably, these CO vibrational frequencies are distinct from chemisorbed CO on the (100) or (111) surfaces of Rh.<sup>22</sup> At the end of series 2 (the 21<sup>st</sup> min of the series 2 in Figure 6b), the flowing CO was replaced with flowing He; the progressive decrease of CO concentration in series 3 resulted in the restructuring of  $\text{Rh}_3(\text{CO})_3$  to Rh clusters without CO ligand. The series 1 (under non-steady state catalytic condition) and series 3 (under the same temperature and CO pressure as DFT modelling) exhibit the same evolution of CO vibrational features, suggesting that CO pressure is the main driving force, regardless of CO produced from  $\text{CH}_4$  reforming or from external environment. Overall, the formation and restructuring of the Rh active site,  $\text{Rh}_3(\text{CO})_n$  can be reversed by changing the chemical potential of CO surrounding the catalytic site.

In conclusion, this work demonstrated that the structure of the Rh nanoclusters supported on  $\text{CeO}_2$  evolves depending on the partial pressure of product CO in the gas environment to which the catalyst is subjected. Beyond the Rh/ $\text{CeO}_2$  catalyst studied in our work, the restructuring

capability of CO on metal catalysts has been shown in systems where CO was a reactant.<sup>3-5,23</sup> CO has been found to induce the restructuring of stepped Pt surfaces to CO-covered Pt clusters with size of 2.1-2.2 nm.<sup>4</sup> For Cu, a metal with a weaker cohesive energy than Pt, CO can even fragment the close-packed Cu(111) surface into nm-sized CO-covered clusters that can activate H<sub>2</sub>O.<sup>23</sup> In our system, the singly dispersed Rh cations in the as-prepared catalyst transform to Rh NPs after reduction by H<sub>2</sub>, but CO, a product formed from steam reforming of methane, can re-disperse Rh atoms of the Rh NPs into catalytically active CO liganded Rh<sub>3</sub> clusters during catalysis. As evidenced by first principles atomistic thermodynamic calculations and *in situ/operando* spectroscopy, the CO product gas produced by the SRM plays a crucial role in inducing and maintaining the highly dispersed active sites, Rh<sub>3</sub>(CO)<sub>n</sub> of this Rh/CeO<sub>2</sub> catalyst. This work demonstrates the necessity of including product molecules as a factor in identifying the active sites under catalytic conditions.

## **Methods:**

### **Catalyst Synthesis**

CeO<sub>2</sub> nanorods were synthesized by a hydrothermal method as reported in literature.<sup>24-26</sup> In a typical synthesis, 1.736 g Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Aldrich, 99.99%) was dissolved in 10 mL deionized water, then was added to a concentrated NaOH solution drop wisely, forming a mixed solution of Ce(NO<sub>3</sub>)<sub>3</sub>. The concentrated NaOH solution was prepared by dissolving 19.2 g NaOH (Aldrich, >98%) in 70 mL DI water. Then, the mixed solution of Ce(NO<sub>3</sub>)<sub>3</sub> was kept under vigorous stirring for 30 min before transferring to a Teflon-lined stainless-steel autoclave for hydrothermal treatment at 100 °C for 24 hrs. Upon the hydrothermal synthesis, the autoclave was cooled to room temperature. Then, the obtained yellow powder was washed by deionized water until its pH is

neutral. Finally, the powder was dried at 60 °C in air for 10 hrs. This sample of CeO<sub>2</sub> nanorod was used as a support in the following preparation of Rh<sub>1</sub>/CeO<sub>2</sub> catalyst.

The Rh<sub>1</sub>/CeO<sub>2</sub> catalyst was prepared by the deposition-precipitation method.<sup>27</sup> In a typical synthesis, 1.00 gram of CeO<sub>2</sub> nanorods was dispersed in 50 mL of deionized water. The mixture was sonicated for 10 mins and stirred at 400 rpm for 1hr. Here it is called CeO<sub>2</sub> aqueous dispersion. Then, 5.6 mg of rhodium (III) nitrate hydrate (Aldrich, ~36% rhodium basis) which provided about 2.0 mg Rh metal was weighted and then dissolved in 20 mL DI water. The prepared rhodium salt solution was slowly introduced into the prepared CeO<sub>2</sub> aqueous dispersion by a syringe pump at a flow rate of 0.2 mL/min while the aqueous solution was being stirred, making an aqueous mixture containing both Rh<sup>3+</sup> and CeO<sub>2</sub> nanorods. This aqueous mixture of Rh<sup>3+</sup> and ceria nanorods was continuously stirred for an additional 3 hrs. The pH value of the mixture was carefully adjusted to 9.5 by gradually introducing an ammonium hydroxide solution (Aldrich, 28%) while the aqueous mixture was being stirred, followed by continuous stirring for an additional 5 hrs. Then, the aqueous mixture was centrifuged at 3000 rpm for 5 mins. After the centrifugation, the upper layer was decanted. The obtained solid product was dried at 60 °C in oven overnight and calcined in a muffle furnace at 250 °C for 2 hrs to obtain the as-synthesized Rh<sub>1</sub>/CeO<sub>2</sub> catalyst. The actual loading of Rh on CeO<sub>2</sub> nanorods of the as-synthesized catalyst was measured with ICP-AES, which was found to be 0.17wt%. Thus, either 0.17wt% Rh/CeO<sub>2</sub> or Rh<sub>1</sub>/CeO<sub>2</sub> was interchangeably used to denote the as-synthesized catalyst in the following sections.

### **Catalytic Tests**

The catalyst (50 mg) was mixed with 300 mg of quartz for the steam reforming of methane. Catalytic performance of the Rh<sub>1</sub>/CeO<sub>2</sub> catalyst was evaluated in a fixed-bed flow reactor in the temperature range of 350-600 °C. A K-type thermal couple was inserted into the catalyst bed to

monitor the reaction temperature. The temperature was controlled by a PID controller. The catalyst was pretreated in H<sub>2</sub> (5% in Ar, 20 ml/min) at 500 °C for 1 hr before catalysis. Water was introduced by a syringe pump in the form of water vapor formed through a vaporization chamber held at 120 °C before entering reactor. The mole flow rate of water was kept at two times of that of methane. CH<sub>4</sub> (10% in Ar, 20 mL/min) was pre-mixed with water vapor before flowing into the reactor. To make sure water vapor can be fully delivered to the catalyst bed, all stainless-steel tubing and valves between the vaporization chamber and the reactor was heated and preserved at 120 °C during evaluation of catalytic performance. The products were analyzed by an on-line GC equipped with a Hayasep-D column and a TCD detector. The conversion of CH<sub>4</sub> and yield to H<sub>2</sub> were evaluated by the equations below. The  $[CH_4]_{in}$ ,  $[CH_4]_{out}$ , and  $[H_2]_{out}$  stand for the CH<sub>4</sub> concentration at the inlet to the reactor, the CH<sub>4</sub> and H<sub>2</sub> concentration at the outlet of the reactor, respectively.

$$Conversion(CH_4) = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{in}} \times 100\% \quad (1)$$

$$Yield(H_2) = \frac{\frac{1}{3}[H_2]_{out}}{[CH_4]_{in}} \times 100\% \quad (2)$$

### Catalyst Characterization

The *in-situ* XAS experiments were mainly performed at beamline BL36XU at SPring-8. The Rh K-edge signal was collected under fluorescence mode by a Ge detector. The data was calibrated, merged and analyzed using the Athena and Artemis software package with the standard protocol.<sup>28</sup> For the *in-situ* experiment, the catalyst powder was loaded in a capillary quartz tube cell.<sup>29</sup> Then, gas was introduced into the cell, and their flow rates were controlled by mass flow controllers. In terms of reduction, 20 ml/min of 5% H<sub>2</sub> was introduced to the reactor. Regarding to

catalysis, the composition of reactant mixture of steam reforming of methane was CH<sub>4</sub> (2.5 ml/min), He (22.5 ml/min) and water vapor. The cell was heated and then kept at a desired temperature for half an hour in flowing 5% H<sub>2</sub> for reduction or mixture of reactants for steam reforming of methane, and then the Rh K-edge spectrum was collected *in-situ* in the flowing gas at about 150°C. For the fitting of Fourier transformed EXAFS data, the coordination number (CN), distance (Å) and Debye-Waller factor ( $\sigma^2$ ) were set as variables. The wavelet transformed analysis of EXAFS data was performed with HAMA Fortran package from the ERSF website. Parameters used in these WT analyses were the Morlet function,  $\sigma = 1$ , and  $\kappa = 5$ . The full details are described in Supplementary Note 1.

Surface chemistries of the catalyst under reduction and catalysis conditions were tracked with a commercial ambient pressure X-ray photoelectron spectrum (AP-XPS) system.<sup>30</sup> The reaction cell is integrated into a monochromatic Al K $\alpha$  X-ray source and an energy analyzer with a precise geometry. The mixture of reactant gases at Torr pressure with ratio of partial pressure of CH<sub>4</sub> and H<sub>2</sub>O vapor at 1:2 was introduced to the reaction cell through a gas manifold which was remained at a temperature 120-150 °C for delivery of water vapor to the reaction cell. The partial pressures of CH<sub>4</sub> and H<sub>2</sub>O (vapor) were 0.5 Torr and 1.0 Torr, respectively. The total flow rate of gas mixture entering the in-situ reaction cell was ~ 4 ml/min.<sup>30</sup> The total pressure of reactant gases in the reaction cell was the average value of the measured pressures by a capacitance gauge located between the gas manifold and tubing to the entrance port of the reaction cell and another capacitance gauge placed between the tubing of exit port of the reaction cell. The XPS data was analyzed by the CasaXPS software. All the spectrum peaks were calibrated by Au 4f<sub>7/2</sub> peak to 84.0 eV. Ce3d spectra are deconvoluted to ten components, whereas six peaks at 882.6 eV, 889.0 eV, 898.6 eV, 900.9 eV, 907.7 eV and 916.9 eV are assigned to v, v'', v''', u, u'', and u''' of Ce<sup>4+</sup>,



respectively and four at 880.6 eV, 885.2 eV, 899.2 eV, 904.0 eV are assigned to  $v_o$ ,  $v'$ ,  $u_o$ , and  $u'$  of  $Ce^{3+}$ , respectively.<sup>31</sup>

DRIFTS spectra of CO molecules absorbed on the catalyst using guest CO source were collected on a Thermal-Fisher Nicolet iS50 FTIR spectrometer using an MCT/A detector with a spectrum resolution of  $4\text{ cm}^{-1}$  integrated with a diffuse reflectance reaction cell (Praying Mantis high-temperature reaction cell) at our collaborators' labs at FZU. A home-made gas inlet system, including a six-way valve, was used to perform transient studies. Here, we call it an *ex-situ* study to distinguish from the *operando* studies to be described in the following. The purpose of this *ex-situ* study is to identify the chemical state and dispersion of Rh atoms of the as-synthesized catalyst 0.17wt%Rh/CeO<sub>2</sub>. In this *ex-situ* study, the catalyst was mounted in the cell without dilution. It was pretreated in the flow of helium (99.999%) to remove surface adsorbates before the experiment of *ex-situ* studies. Different from these *ex-situ* DRIFT studies, *operando* DRIFT experiments were performed to identify CO stretching frequency of active sites of the catalyst formed during SRM catalysis and whether this active site could restructure under different partial pressure of CO. The experimental protocol is summarized in Supplementary Note 4.

Morphology, size and distribution of single atoms of as-prepared 0.17wt%Rh/CeO<sub>2</sub> samples, samples upon different pretreatment or after catalysis were examined with advanced TEM instruments at our collaborators' labs including FZU (Supplementary Note 5). In a typical sample preparation, 10 mg of the catalyst powder was dispersed in 50 ml anhydrous ethanol and then sonicated for 5 mins. Then, 50  $\mu\text{l}$  of the liquid suspension was drop casted on a copper mesh (300 mesh) with carbon nano-film. The copper mesh with sample was dried overnight before loaded on the sample stage for TEM. The morphology and lattice fringes of ceria could be observed.

## DFT Calculations

Periodic DFT calculations were performed with the Vienna ab-initio simulation package (VASP), version 5.4.1.<sup>32-34</sup> The exchange-correlation energy was calculated using the Perdew-Burke-Ernzerhof functional.<sup>35</sup> Spin polarization was used in all calculations. A dipole correction in the z direction was used for surface calculations. The projector-augmented wave (PAW) method was used to describe the core electrons.<sup>36,37</sup> The Kohn-Sham orbitals were expanded using a set of plane waves with kinetic energy up to 600 eV. The electronic structure was considered converged when the electronic energy difference between consecutive SCF steps falls below  $10^{-6}$  eV. The surface and molecular structures were considered converged when the Hellman-Feynman forces on atoms fall below 0.02 eV/Å. To correct for the self-interaction error of the Ce 4f electrons, a Hubbard-like on-site repulsion term was added using the approach of Dudarev et al. (DFT+U), with  $U_{eff} = U - J = 4.5$  eV.<sup>38,39</sup> Using a parabolic equation of state, the lattice parameter of CeO<sub>2</sub> was found to be 5.502 Å, close to reported values.<sup>40</sup>

$(2 \times 2)$ ,  $(\sqrt{7} \times \sqrt{7})$ ,  $(3 \times 3)$ ,  $(3 \times \sqrt{7})$  and  $(4 \times 4)$  unit cells of CeO<sub>2</sub>(111) containing 3 O-Ce-O tri-layers were used in the calculations.<sup>40-42</sup> For these periodicities, the Brillouin zone was sampled using  $(3 \times 3 \times 1)$ ,  $(3 \times 3 \times 1)$ ,  $(2 \times 2 \times 1)$ ,  $(2 \times 2 \times 1)$ , and  $(2 \times 2 \times 1)$  gamma-point-centered  $k$ -meshes respectively.<sup>43</sup> The sensitivity of stable surface structures on the choice of  $U_{eff}$  was assessed by calculations using another  $U_{eff}$  value (3.67 eV) benchmarked against single point calculations using the HSE06 hybrid functional.<sup>44,45</sup> Single point HSE06 calculations were performed from converged PBE+U ( $U_{eff} = 4.5$  eV) geometries. The Brillouin zone was sampled using a 2-fold reduced (VASP commands: NKREDX = 2, NKREDY = 2), gamma point centered

( $2 \times 2 \times 1$ ) mesh.<sup>46</sup> The ( $3 \times 3$ ) cell was used to simulate the Rh active sites. The bottom tri-layer was constrained to bulk positions in structural optimizations.

Vibrational modes were calculated using the finite difference method with a step size of 0.015 Å. Factors of 0.9828 and 1.0086 were multiplied to OH and CO stretching modes respectively when comparing calculated vibrational frequencies to experimental values. Core level shift calculations were performed using both the initial state approximation (ISA) and the final state approximation (FSA). In the ISA, the vacuum-aligned Rh 3d eigen energies are directly compared to each other. Lowering the Rh 3d eigen energy results in a positive CLS. In the FSA, one 3d electron is assumed to be excited by absorption of the incident photon. The core electron binding energy ( $E_{CL}$ ) is defined as  $E_{CL} = E(N-1) - E(N)$ , where  $E(N-1)$  is the energy of the assessed structure after excitation, and  $E(N)$  is the energy before excitation.<sup>47</sup> The final state CLS is computed by taking the difference between the  $E_{CL}$  of the assessed structure and the  $E_{CL}$  of a Rh atom in the 3<sup>rd</sup> layer below the surface of a 7-layer ( $3 \times 3$ ) Rh(111) slab. For reference, by the final state approximation, the CLS of a bulk-like Rh<sup>3+</sup> ion below the Rh<sub>2</sub>O<sub>3</sub>(0001) surface is 0.99 eV.

### **Modeling the Ceria Surface and the Rh Active Sites.**

The most stable CeO<sub>2</sub>(111) surface structure under reaction conditions was determined by minimizing surface free energy under the reaction gas environment (Figure 3 and Supplementary Figure 24).<sup>48,49</sup> The Ce<sup>3+</sup>: Ce<sup>4+</sup> ratio was limited to 1:1 in the two outermost CeO<sub>2</sub> tri-layers to simulate surface reduction. Surface and subsurface O<sub>vac</sub> and adsorbed H on surface O were included as the possible surface motifs. Bulk CeO<sub>2</sub>, H<sub>2</sub> gas and H<sub>2</sub>O gas were used as Ce, H, and O reservoirs in calculating surface free energy (Supplementary Note 6). The simulated Rh active sites were compared to each other by their Gibbs free energies of formation, normalized by each

site's Rh nuclearity.<sup>50,51</sup> For a given Rh site, the hydroxylated CeO<sub>2</sub>(111) surface, H<sub>2</sub> gas, H<sub>2</sub>O gas, CO gas and hypothetical supported Rh<sub>13</sub> clusters were chosen as the Ce, H, O, C, and Rh reservoirs (Supplementary Note 6).

The thermodynamically controlled assumption of the CeO<sub>2</sub>(111) surface structure was made based on reported experimental observations and reported reaction barriers of elementary redox processes.<sup>52-54</sup> Reduced CeO<sub>2</sub>(111) surfaces in (3 × 3) periodicity were searched based on rules developed from observations in literature and patterns found for representative surfaces.<sup>40-42,55-61</sup> First, using the s-xyz-w notation of Murgida et al., the most stable O<sub>vac</sub>-containing surfaces should contain minimal x+y+z and w. Second, when OH groups and O<sub>vac</sub> coexist, the two prefer to segregate. Third, when multiple vacancies are present, Ce<sup>3+</sup> ions prefer to cluster near a single vacancy. Fourth, Ce<sup>3+</sup> ions prefer to localize near OH groups. And fifth, Ce<sup>3+</sup> ions near an O<sub>vac</sub> prefer to stay out of the O<sub>vac</sub>'s first coordination shell.

For a given stoichiometry, all structure combinations were first generated without considering the arrangement of Ce<sup>3+</sup> ions, sorted by rules 1 and 2 and optimized without specification of initial magnetic moments. The most stable structures found using this method were selected, and favorable Ce<sup>3+</sup> localization patterns were generated and optimized using rules 3, 4, and 5. In this set of calculations, a set of plane waves with kinetic energy up to 400 eV was used, the Brillouin zone was sampled using only the Gamma point, the electronic energy difference between consecutive SCF steps was converged to 10<sup>-5</sup> eV, and the forces on atoms were converged to below 0.05 eV/Å.

The Rh active sites were searched by first computing the ligand-free Rh single atom or cluster binding sites on the fully hydroxylated surface, then checking the possible CO/H ligand configurations on the stable Rh sites. A small representative set of OH-liganded Rh<sub>1</sub>, Rh<sub>2</sub>, and Rh<sub>3</sub>

structures were optimized as well, but we did not find them to be as stable as CO or H-liganded Rh single atoms and clusters. In this set of calculations, a set of plane waves with kinetic energy up to 450 eV was used, the electronic energy difference between consecutive SCF steps was converged to  $10^{-6}$  eV, and the forces on atoms were converged to below 0.05 eV/Å.

The surface energy or Gibbs free energy of formation of each structure consists of the translational & rotational components of their gas constituents and vibrational components of the gas constituents and corresponding surface motifs (Supplementary Note 7 and Supplementary Figures 10-16). For supported Rh sites, the configurational entropy of Rh (Supplementary Note 8 and Supplementary Figure 17), the chemical potential of Rh atoms (Supplementary Note 9 and Supplementary Figures 18 and 19), and a back bonding-based penalty for the adsorption energy of CO (Supplementary Note 10 and Supplementary Figure 20 and 21) were included as well.

Vibrational contributions to Gibbs free energy were computed in two ways (Supplementary Note 7). In the screening of CeO<sub>2</sub> surface structures and supported Rh sites and the construction of Figures 3 and 5, vibrational contributions were estimated based on the formation of six types of motifs: surface & subsurface O vacancies, H adsorbed on surface O, H adsorbed on Rh, and CO adsorbed on Rh pointing towards or away from the surface. The average margin of error of this approach was up to  $k_B T$  per motif from the harmonic oscillator approximation (Supplementary Figure 16). To construct the final T/P<sub>CO</sub> stability diagram of Rh sites (Figure 4), the harmonic oscillator approximation was used instead.

Rh<sub>13</sub> was chosen as the Rh chemical potential reference due its resemblance to the Rh coordination environment found by EXAFS after H<sub>2</sub> pretreatment.<sup>62</sup> The Rh chemical potential was computed based on the cohesive energy of the Rh<sub>13</sub> cluster, its Gibbs free energy of adsorption, and the configurational entropy of Rh<sub>13</sub> clusters (Supplementary Note 9).

It is well-known that the PBE functional overpredicts the strength of transition metal d state-CO  $2\pi^*$  orbital back bonding.<sup>63</sup> Many methods have been employed to correct this problem.<sup>64-66</sup> Here, the singlet-triplet transition energy ( $\Delta E_{ST}$ )-based method of Sumaria et al. was developed and employed for the Rh active sites, where a linear trendline was fitted between the CO adsorption energy correction and the relaxed C-O bond length (Supplementary Note 10).<sup>67</sup> The CO adsorption energy correction brings the CO adsorption energy values closer to those obtained from higher level calculations.<sup>68</sup>

**Data availability:** Atomic structures of CeO<sub>2</sub>(111) surfaces appearing on Figure 3a and CeO<sub>2</sub>(111)-supported Rh clusters used to construct Figure 4a are available in supplementary data. Other data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request. Information request on experimental (resp. theoretical) data should be addressed to FT (resp. PS).

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### **Author contributions**

PS and FT conceptualized and supervised the work. GY performed the computational studies. YT, YTL, YXL and LN performed the experiments. YT, LN, TS and KH contributed to the EXAFS experiments. FT guided the experimental studies. The draft was prepared and edited by GY, YT, FT, and PS.

### **Competing interests**

Authors declare that they have no competing interests.

### **Figure legends and captions**

**Fig. 1. Evolution of the coordination environment of Rh.** Fourier-transformed  $k^2$ -weighted  $r$ -space spectra of (a) as-synthesized 0.17 wt% Rh/CeO<sub>2</sub> in air, (b) catalyst at 500 °C in 5% H<sub>2</sub> (20

ml/min), and (c) *in situ* study of 0.17wt% Rh/CeO<sub>2</sub> under catalytic conditions at 500 °C (2.5 ml/min CH<sub>4</sub>, 22.5 ml/min He, and water vapor). Although the height of the Rh-Rh peak grows after the H<sub>2</sub> pretreatment, it decreases during the SRM reaction.

**Fig. 2. Surface chemistry of Ce and O during H<sub>2</sub> reduction and catalysis.** AP-XPS studies of the 0.17 wt% Rh/CeO<sub>2</sub> catalyst reduced by 0.5 Torr H<sub>2</sub> at 500 °C (a-b) and during SRM ( $P_{CH_4} = 0.5$  Torr and  $P_{H_2O} = 1.0$  Torr) at 500 °C (c-d). The Ce 3d spectra (a and c) and O 1s spectra (b and d) are deconvoluted. Peak positions of the deconvoluted peaks are listed in Supplementary Table 2. The peak at 535.4 eV is the O 1s peak contributed from CO or/and H<sub>2</sub>O in gas phase. The surface of the Rh/CeO<sub>2</sub> catalyst is largely reduced in the H<sub>2</sub> pretreatment and catalytic conditions.

**Fig. 3. Structure and stability of the CeO<sub>2</sub>(111) surface under gas pressure of H<sub>2</sub> and H<sub>2</sub>O vapor.** (a) Surface structures formed in a gas environment of H<sub>2</sub> and H<sub>2</sub>O at different chemical potentials. (b and c) Top and side view of CeO<sub>2</sub>(111) passivated with OH groups, corresponding to zone 1C in (a). (a) consists of three main phases, including solely hydroxylated regions (1A, 1B, 1C: 2.54, 5.09, 7.63 OH/nm<sup>2</sup>, beige-colored regions; a coverage of 4.24 OH/nm<sup>2</sup> is stable in a sliver between regions 1A and 1B), OH/O<sub>vac</sub> mixed regions (2A: 0.85 O<sub>vac</sub>/nm<sup>2</sup> & 1.70 OH/nm<sup>2</sup>, 2B: 0.85 O<sub>vac</sub>/nm<sup>2</sup> & 2.54 OH/nm<sup>2</sup>, 2C: 3.39 O<sub>vac</sub>/nm<sup>2</sup> & 0.85 OH/nm<sup>2</sup>, magenta-colored regions), and solely O<sub>vac</sub>-containing regions (3A: 1.91 O<sub>vac</sub>/nm<sup>2</sup>, 3B: 3.39 O<sub>vac</sub>/nm<sup>2</sup>, cyan-colored regions). The olive-colored hatched region is associated to possible pressure under which SRM could be performed, from  $P_i \sim 10^{-2}$  bar to  $P_i \sim 10^1$  bar; the steady state SRM gas environment at 500 °C is marked as a red dot ( $\Delta\mu_{H_2} = -1.17$  eV,  $\Delta\mu_{H_2O} = -1.65$  eV, calculated using the translational and rotational



contributions, assuming  $P_{H_2} = 0.14$  bar and  $P_{H_2O} = 0.11$  bar). The reaction condition falls in the region where the  $CeO_2(111)$  surface is hydroxylated.

**Fig. 4. Structure and stability of Rh active sites.** Theoretical modeling of the evolution of the Rh active site under catalytic conditions as a function of catalysis temperature (T) and CO pressure ( $P_{CO}$ ) by holding the chemical potentials of gas phase  $H_2$  and  $H_2O$  constant as those during SRM at 500 °C (See Fig. 3). (a) Theoretically proposed stable Rh species; the SRM condition at 500 °C ( $P_{CO}=0.045$  bar) is marked with a green dot with bars representing possible variations in T and  $P_{CO}$ . As CO pressure decreases,  $Rh_3(CO)_3$  transforms to  $Rh_3(CO)_2$  and then  $Rh_3H_1$ . (b) Gibbs free energy of formation of the most stable Rh-based sites as a function of catalysis temperature (T) and CO pressure ( $P_{CO}$ ); the full black line marks the transition between supported Rh nanoparticles and highly dispersed  $Rh_m(CO)_n$  clusters, below which the  $Rh_m(CO)_n$  species is more stable than the Rh nanoparticle. We find the  $Rh_3(CO)_3$  cluster to be close to the Rh nanoparticle in stability under catalytic conditions. For reference, the stability of the  $Rh_3(CO)_3$  site is shown in Supplementary Figure 26. (c-g) Atomic-scale geometries of Rh sites present in (a). (c)  $Rh_3H_1$ . (d)  $Rh_3(CO)_2$ , (e)  $Rh_3(CO)_3$ , (f)  $Rh_3(CO)_4$ , and (g)  $Rh_1(CO)_2$ .

**Fig. 5. Relative stability of  $Rh_m(CO)_n$  sites in the reaction environment.** The ensemble of Rh sites generated during the SRM reaction at 500 °C (see Fig. 4), ordered by Gibbs free energy of formation relative to the most stable  $Rh_3(CO)_3^+$  site (line color/site type: gray/ $Rh_3$ ; blue/ $Rh_2$ ; red/ $Rh_1$ ). A  $3k_B T$  region is shaded in green to indicate the thermally accessible structures. The  $Rh_3(CO)_3$  clusters are more stable than  $Rh_2(CO)_3$  and  $Rh_1(CO)_2$  sites in the reaction environment.

**Fig. 6. Reversible restructuring of the Rh active sites.** CO product pressure-driven restructuring of Rh catalytic sites. (a) Three series of variations of CO pressure at 500 °C marked on the theoretical  $P_{CO}$ -T phase diagram (upper portion adopted from Fig. 4a). (b) DRIFTS spectra (b1-b9) at 500 °C under SRM catalytic condition. Series 1: b1-b9, a transient pulse of CH<sub>4</sub> reactant (equivalent to 0.1 ml CH<sub>4</sub>, STP) composed of 1% CH<sub>4</sub> and 99% Ar was introduced to the catalyst by mixing the pulse with flowing water vapor formed by flowing Ar (99.999%) through water of 25°C. No external CO source was introduced before and during Series 1. Series 2: b10-b14, spectra in a flow of CO (1%) balanced with Ar. Series 3, spectra (b15-b20) being purged with argon as a function of time. The background spectrum for DRIFTS study was collected on the catalyst surface under Ar and water vapor flow at 500 °C. In Series 1, 20 ml/min of water vapor containing 3% vapor was continuously flowing through the reaction cell, CH<sub>4</sub> gas (1% CH<sub>4</sub> in Ar) was pulsed to mix with water vapor. The DRIFTS spectra were taken as a function of time without CH<sub>4</sub> in the flow. At the t=2 min (b1), the vibrational features in the 2050-1850 cm<sup>-1</sup> region, assigned to Rh<sub>3</sub>(CO)<sub>3</sub>, were clearly observed as CO was generated from SRM at 500°C. These experiments overall show the formation of Rh<sub>3</sub>(CO)<sub>3</sub> to be reversible.

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